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## Highly stable silver nanoparticles for SERS applications

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**Abstract.** Plasmonics sensor configurations utilizing localized plasmon resonances in silver nanostructures typically suffer from rapid degradation of silver in ambient atmospheric conditions. In this work, we report on the fabrication and detailed characterization of ensembles of *monocrystalline* silver nanoparticles (NPs), which exhibit a long-term stability of optical properties under ambient conditions without any protective treatments. Ensembles with different densities (surface coverages) of size-selected NPs (diameters from 12.5 to 24 nm) on quartz substrates are fabricated using the cluster-beam technique and characterized by linear spectroscopy, surface-enhanced Raman scattering microscopy as well as transmission electron, helium-ion and atomic force microscopies. It is found that the fabricated ensembles of monocrystalline silver NPs preserve their plasmonic properties (monitored with optical spectroscopy) and strong field enhancements (revealed by surface enhanced Raman spectroscopy) at least 5 times longer as compared to chemically synthesized silver NPs with similar sizes. The obtained results are of high practical relevance for the further development of sensors, resonators and metamaterials utilizing plasmonic properties of silver NPs.

### 1. Introduction

Light interaction with nanostructures, especially those fabricated of noble metals, gives rise to various fascinating optical phenomena [1]. One of the current research directions in nano-optics is the development of metal nanostructures that efficiently interconvert propagating and localized optical fields and thereby facilitate the generation of strongly enhanced local electrical fields. Field enhancements (FEs) occur due to resonantly excited surface plasmons, representing collective electron oscillations in metals coupled to electromagnetic fields in neighboring dielectrics [2]. Strong FEs are



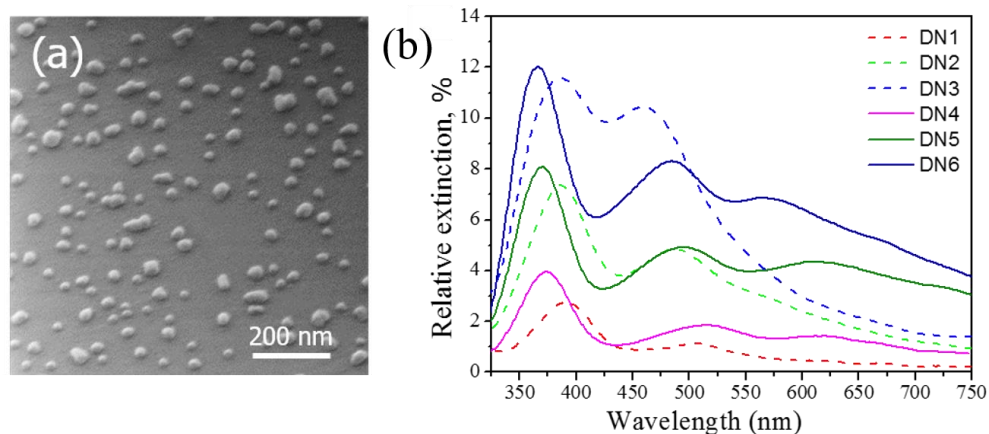
extremely important for practical applications for example in sensing and catalysis as well as in surface-enhanced Raman scattering (SERS) [3, 4]. Noble metal nanostructures are also very promising for the formation of surface plasmon resonators, which have demonstrated enormous enhancement of the fluorescence of quantum emitters, thus facilitating the development of ultra-bright and stable single-photon sources. In addition, they can be used as real-time sensors, plasmonic solar cells, building blocks for light-energy guiding devices and metamaterials with unique optical properties, *etc.* Silver exhibiting excellent plasmonic properties<sup>5</sup> can advantageously be used in the majority of the above-mentioned applications [5-6].

There are many strategies for the fabrication of plasmonic structures using silver. Different approaches such as particle formation by evaporation or sputtering, high-fluency ion implantation, chemical and photo reduction, production of colloid nanoparticles (NPs), *etc.* were suggested. Many of them allow formation of nanomaterials with an attractive efficiency. However, rapid oxidation/sulfidation from the ambient atmosphere dramatically decreases all bonuses of this metal [7, 8] and causes complications in terms of practical applications. For example, the sensors containing Ag usually require storage in inert gases and the operational time of such devices in the ambient atmosphere is rather limited. One existing solution is to make a protection layer, which can prevent the Ag structures from the degradation due to reactions with environmental species. However, these treatments are not always applicable or rather complex to be used on an industrial scale. A possible approach to solve this problem could be the formation of very pure particles with perfect crystalline structure. They should be more stable against the above-mentioned degradation phenomena. A very promising approach for preparation of such NPs is aggregation of metal atoms into clusters from very pure sources in vacuum. These clusters can be collimated into beams, size selected and deposited or implanted on/in different substrates, which provides great capabilities for controlling the structure and properties of materials on the nanoscale [9]. In this work, we utilize a cluster beam deposition technique based on magnetron sputtering [10] as a method of fabrication of ensembles of monocrystalline Ag NPs with well-controlled sizes. Due to these properties they demonstrate excellent stability of plasmon band intensity (it decreases only for about 20% after 30 days) and strong FE which is also preserved over rather long time period at room temperature and ambient atmosphere. We anticipate that the obtained results are very promising for sensor applications.

## 2. Experimental section.

### 2.1. Ag NPs by a cluster beam deposition technique

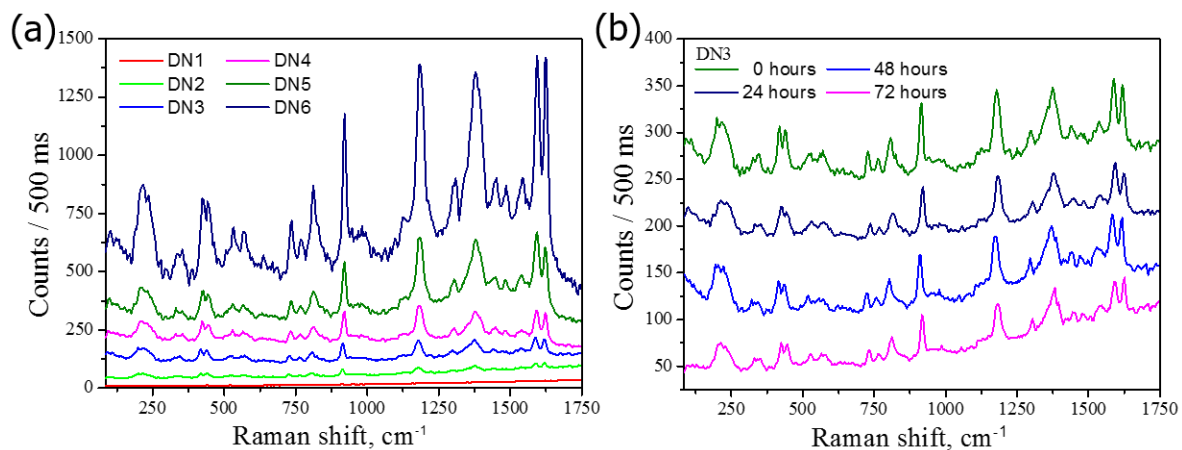
A magnetron sputtering NPs apparatus (MaSCA) [10] utilizing a commercial source, NC200U from Oxford Applied Research, was used for cluster production from silver targets of 99.99% purity. In the source, the target material was sputtered by an Ar plasma and was condensed into NPs of various sizes in the aggregation region with the help of He as a buffer gas. Thereafter, the NPs were expanded through a nozzle and collimated into a beam. NPs from a beam were selected using an electrostatic quadrupole mass selector (EQMS). Only charged particles were selected and steered toward deposition on 10x10 mm<sup>2</sup> quartz substrates in the vacuum with a background pressure of approximately  $5 \times 10^{-7}$  mbar. The size-selection was performed at two different EQMS voltages of 300 and 1600 V. According to earlier studies, these voltages correspond to mean particle diameters of  $12.5 \pm 1.1$  and  $24.0 \pm 2.0$  nm, respectively. Particles of these sizes are further referred to as small and large NPs. The size-selected silver NPs were deposited in a so-called soft-landing regime securing that the cluster kinetic energy is much smaller than the cohesive energy of atoms leading to no or very small distortion of the particles shape, which is supposed to be close to spherical in a free cluster beam. Samples were prepared with several different particles coverages (surface densities of NPs) ranging between approximately 300-600 particles/ $\mu\text{m}^2$  for small NPs (samples DN1-DN3) and 70-300 particles/ $\mu\text{m}^2$  for large NPs (samples DN4-DN6). Figure 1 shows HIM image and linear spectra of the fabricated samples.



**Figure 1.** (a) HIM image of deposited large silver NPs (24 nm). (b) Experimental extinction spectra for the ensembles of small (dashed lines) and large (solid lines) Ag NPs with three different surface densities.

## 2.2. SERS characterizations

In order to estimate the applicability of the samples for SERS, the SERS characterizations are performed. The measurements are carried out on the samples kept in the air for 8 days after the fabrication. All samples are covered by an ethanol  $10^{-6}$  M solution of Crystal Violet (CV) dye and dried under ambient conditions. As shown elsewhere, the oxidation of silver NPs or other reactions with species present in air typically lead to significant decrease or completely disappearing SERS signal on a relatively short time scale of a few days [11-12]. The typical SERS spectra are shown in Figure 2 and they demonstrate considerable or even high intensity depending on particle size and surface coverage. SERS images show rather homogeneous signal distribution across the samples except a few fluctuations in intensity related to cluster diffusion and aggregation around natural surface defects of quartz. As can be seen from the spectra presented in Figure 2a, the SERS intensity increases with increasing cluster density from DN1 to DN3 and from DN4 to DN6.



**Figure 2.** SERS spectra (a) for the samples DN1-DN6 obtained 8 days after the deposition of small and large Ag clusters on the glass substrate (particles surface density increases from DN1 to DN3 for the small NPs (12.5 nm) and from DN4 to DN6 for the large NPs (24 nm)), (b) for the sample with cluster surface density DN3 and different time durations after coverage by analyte.

This is an obvious tendency because every cluster represents the so-called hot spot, i.e. the place with enhanced local field. Hence, an increase in cluster density gives higher intensity. At the same time, the intensity for the samples with large NPs tends to be much higher compared to the samples with small ones due to the factor of two differences in radius between the small and large NPs yielding 8 times difference in the effective volume for individual particles. Thus, more dye molecules surrounding large clusters become excited and contribute to SERS signal. It is also known that the maximal gain can be expected for specific (efficient) particle size and distances between them. However, study of this phenomenon was not among the scopes of current work. In order to monitor evolution of spectra after covering the silver NPs by the analyte, we performed the measurements each 24 hours. These SERS spectra (see Figure 2b) shows only near 15% decrease of intensity after 72 hours, thus, demonstrating great stability of the cluster ensembles with respect to SERS in ambient atmospheric conditions.

The stability for SERS application of Ag NPs obtained by cluster beam deposition technique is compared with that for the NPs obtained by chemical synthesis. For the comparison of the stability of our clusters for SERS application, we used colloidal silver nanoparticles with size  $21 \pm 6$  nm. Several samples were prepared using these colloids by drop-casting on the glass substrate. Each sample consists on 3-4 drops located separately on one glass slide. The samples were covered by CV 3, 24, 32, and 48 hours after the drop-casting, respectively; each with the same concentration as used for clusters, and dried under ambient conditions. The level of SERS signals is found to be strong only for the samples covered by the dye 3 and 24 hours after the drop-casting of NPs. The mapping shows homogeneously strong SERS signals across the whole area selected for the scan. For the sample covered by CV 32 hours after the drop-casting, the intensity of spectral peaks is significantly decreased and they nearly disappear for the sample covered by the dye 48 hours after the particle deposition. The mapping made for these two samples shows that the SERS signal is present only on some parts of the scanned area. In order to monitor stability of colloidal NPs *after covering by the analyte*, we performed the measurements each 24 hours, similar to that carried out for the NPs deposited from cluster beams. The SERS spectra show nearly 3 times decrease of intensity after first 24 hours, thus, demonstrating much faster degradation of FE compared to the cluster beam-made particles. To compare a signal increase in SERS, with that in ordinary Raman keeping the same experimental parameters, the analytical enhancement factor (EF expression) is used [13]. The average EF are estimated to be  $\sim 0.05 \times 10^4$  (DN1),  $\sim 0.46 \times 10^4$  (DN2),  $\sim 1.41 \times 10^4$  (DN3),  $\sim 0.25 \times 10^5$  (DN4),  $\sim 0.52 \times 10^5$  (DN5) and  $\sim 1.39 \times 10^5$  (DN6), respectively. We would like to stress that in this case we have used non-resonant dye, whereas for resonant cases the enhancement estimation would be one-to-two orders of magnitude higher. The demonstrated stability of plasmonic properties is caused by the monocrystalline structure of silver NPs revealing strong resistance to oxidation and other reactions with atmospheric gases or typical contaminants (for example, sulfurous compounds) during the storage in ambient atmosphere at room temperature. In addition, it is worth mentioning that the purpose of this work [14] is not optimization of structures to get the highest SERS signal and finding the minimal resolvable concentration of an analyte but rather to estimate the stability and applicability of the prepared cluster ensembles. A simple change of substrate type, for example, substituting quartz by Au or Ag, which allow to excite surface plasmon modes, could significantly increase the signal. The reported results are of high relevance for the fabrication of sensors, resonators and metamaterials utilizing plasmonic properties of silver NPs. This work will be followed by further research in order to optimize parameters of the fabricated ensembles of NPs. In future work we are going to work on the optimization of cluster sizes and surface density in order to reach all benefits from the proposed method of fabrication and combine the current technique with lithography. Furthermore, it is worth mentioning that the samples demonstrate several resonances covering almost all visible spectral intervals and one can vary the spectral position by changing the cluster size and surface coverage.

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